

Hydrogeochemical Evaluation of Groundwater for Drinking and Irrigation Purposes in Avudaiyarkoil Block, Pudukkottai District, Tamil Nadu, India

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Abstract: The purpose of this study is to evaluate the quality of groundwater for drinking and irrigation in the Avudaiyarkoil block of the Pudukkottai district, which is a drought-prone region. Samples were collected from 20 wells on January 2021 and analysed for the water quality parameters, such as pH, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- and F^- . The analysis revealed that SO_4^{2-} is the dominant ion followed by Cl^- , HCO_3^- , Na^+ , Ca^{2+} , Mg^{2+} , K^+ , NO_3^- and F^- with respect to the mean value $292 > 234 > 208.4 > 125 > 100 > 24.75 > 18 > 16.15 > 0.2$. The analytical results were compared with WHO and BIS guideline values to know the groundwater potability and TH, TA, SAR, Na%, RSC, PI, MgC and KI were calculated using the analytical results to identify the suitability of groundwater for irrigation purposes.

Key words: Groundwater, hydrogeochemistry, drinking, irrigation, PCA.

Introduction

Groundwater over drafting by the people in India has increased due to the surface water depletion in summer leading to comprehensive studies on groundwater quality and quantity in different parts of India. Water quality changed during its operation and the following processes were caused by evaporation, transformation, selective growth of plants, oxidation or reduction, cation exchange, mineral dissolution, precipitation, compost manure effluent, pollution and biological processes. The geochemical study of groundwater has initially been studied for different purposes and for the

suitability of groundwater quality, in irrigated areas, when the irrigation return flow recharges the aquifer, the elements such as ions leaving the soil may enter into the aquifer, thus deteriorating the quality of groundwater. This research attempted to evaluate water quality for crop irrigation and drinking purposes by comparing water quality parameters with proposed guideline values and by a variety of evaluating parameters (Al-Mussawi, 2014; Delbari et al., 2016; Kongeswaran and Karikalan, 2016; Thangaraj and Karthikeyan, 2022). Hydrogeochemical analysis can be an effective and efficient technique for critical matching of overall water quality for various purposes and addresses data.

Study Area

The Avudayarkoil block lies in the latitude between $10^{\circ} 10' 34''$ and $9^{\circ} 58' 30''$ and the longitude between $78^{\circ} 54' 30''$ and $79^{\circ} 05' 30''$ (Figure 1). The study area has generally experienced a tropical climate while during April to June is generally hot and dry, pleasant weather condition is from November to January. The average annual rainfall recorded at various rain gauges in the region ranges from 833.40 mm to 1033.8 mm, with an average of 910.8 mm. The geology of the Avudayarkoil block is composed of quaternary silt and clay deposits which forms major water-bearing formations.

Methodology

The groundwater samples were collected from 20 open well and borewells during the month of January 2021. Physico-chemical parameters consisting of TDS (total dissolved solids), EC (electric conductivity) and pH (Hydrogen ion activity) were measured in situ at the field using the potable meter (PCS Testr 35) (Prabakaran et al., 2020; Ramachandran et al., 2020). Ca^{2+} (calcium) and Mg^{2+} (magnesium) were titrimetrically determined by standard EDTA, Cl^- (Chloride) was determined by standard silver nitrate (AgNO_3) titration, HCO_3^- (bicarbonate) was measured by titration against

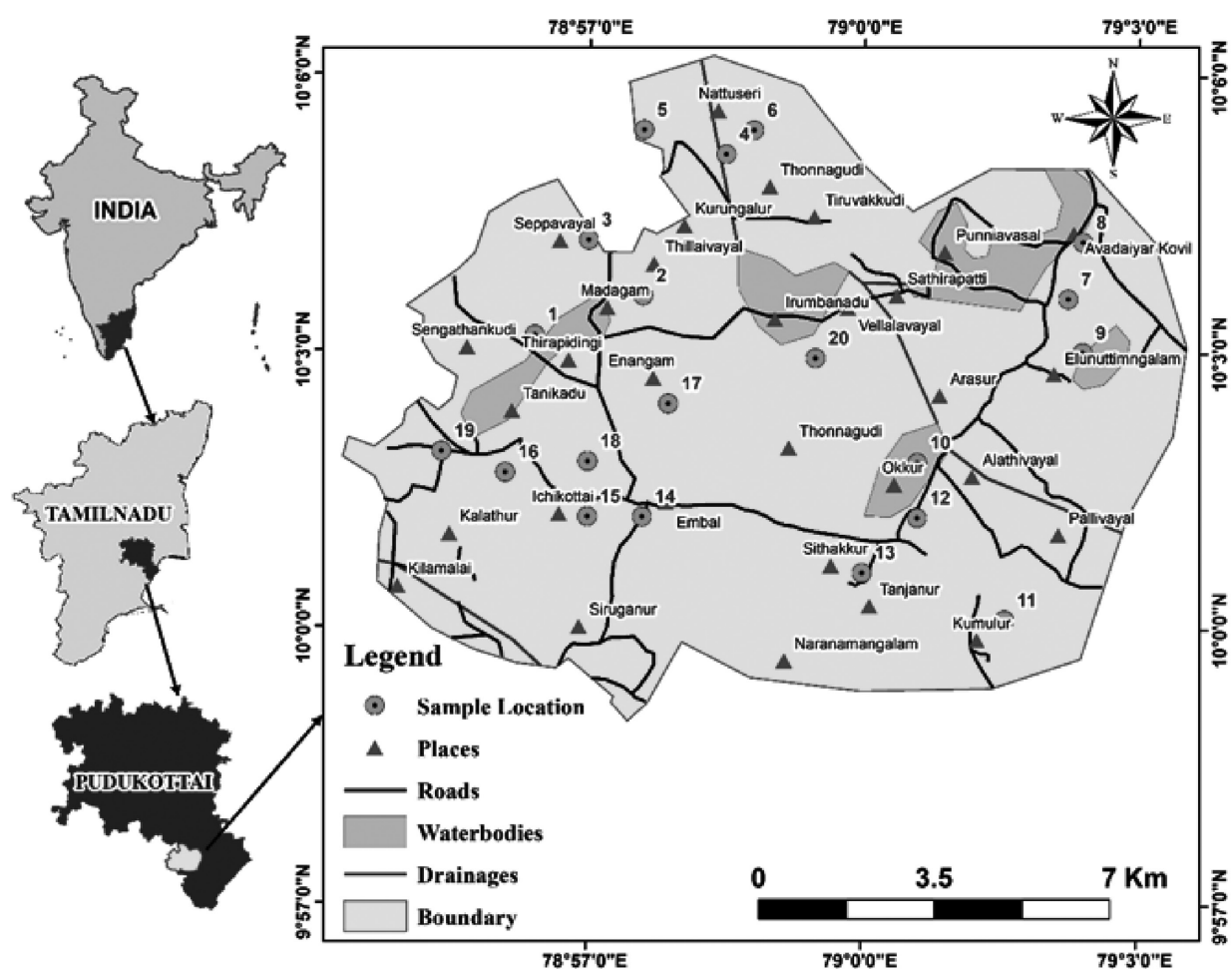


Figure 1: The map shows the study area with sample locations.

hydrochloric acid (HCl), Na^{2+} (sodium) and K^{2+} (potassium) were resolved by Flame Spectrometer (FAAS model AA700) (Muthusamy et al., 2021) and sulphate (SO_4) was determined by the turbidimetric method (UV-Vis spectrophotometer).

Results

The statistical values of analytical results for pH, EC, TDS, major and minor ions in the groundwater samples are given in Table 1. The TDS concentration

Table 1: Analytical result of groundwater samples

<i>Sl. No.</i>	<i>Water quality parameters</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Average</i>	<i>Standard deviation</i>
1	pH	7	8.23	7.45	0.306
2	EC	242	4120	1272	800
3	TDS	163	2884	890	602
4	Ca	24	416	100.00	81
5	Mg	3	94	24.75	19.22
6	Na	22	350	125.00	83.10
7	K	5	50	18.00	12
8	Cl	20	964	234.00	210.00
9	HCO ₃	52	424	208.4	113.16
10	SO ₄	92	810	292.00	150
11	NO ₃	5	39	16.15	8.69
12	F	BDL	0.40	0.20	0.10
13	TA	52	424	250.4	203.52

Table 2: Groundwater quality based on suitability of drinking water purposes

<i>Parameters</i>	<i>Ground water class</i>	<i>Range</i>	<i>Sample</i>	
			<i>In. No</i>	<i>In.%</i>
pH	Excellent	6.5-8.5	20	100
	Poor	>8.5	Nil	Nil
TDS (ppm)	Excellent	0-500	4	20
	Good	501-2000	15	75
	Poor	>2000	1	5
Ca (ppm)	Excellent	0-75	9	45
	Good	76-200	10	50
	Poor	>200	1	5
Mg (ppm)	Excellent	0-30	13	65
	Good	30-100	7	35
	Poor	>100	Nil	Nil
Cl (ppm)	Excellent	0-250	13	65
	Good	250-1000	7	35
	Poor	>1000	Nil	Nil
SO ₄ (ppm)	Excellent	0-200	5	25
	Good	201-400	13	65
	Poor	>400	2	10
NO ₃ (ppm)	Excellent	<45	20	100
	Poor	<45	Nil	Nil
F (ppm)	Excellent	0-1	20	100
	Good	1.1-1.5	Nil	Nil
	Poor	>1.5	Nil	Nil

in the groundwater varied from 163 to 2884 mg/L, while the mean value of TDS was 890 mg/L. Calcium concentrations range from 24 to 416 mg/L, with an average of 100 mg/L whereas Magnesium concentration ranges between 3 mg/L and 94 mg/L, with an average value of 24.75 mg/L. Sodium concentrations range from 22 mg/L to 350 mg/L, with an average value of 125 mg/L. Potassium values range from 5 mg/L to 50 mg/L, with an average value of 18 mg/L. Chloride concentrations range from 20 mg/L to 964 mg/L, with an average value of 234 mg/L. Bicarbonate concentrations vary from 52 mg/L to 424 mg/L, with an average value of 208.4 mg/L. Sulphate concentrations range from 92 mg/L to 810 mg/L, with an average value of 292 mg/L. Nitrate concentration ranges between 5 and 39 mg/L. The average value of nitrate is 15.6 mg/L. F⁻ concentrations varied from the below detectable range to 0.4 mg/L with an average value of 0.2 mg/L.

Discussions

The in-situ measurements of pH, EC and TDS are often giving us the preliminary information that is required in any groundwater study. The pH values are found to be slightly higher in the eastern part of the research area compared to other regions but the values fall well within the permissible limit prescribed by WHO (2017). From the spatial distribution of TDS, it is found that the groundwater quality in the study area is very dynamic. From the spatial distribution diagram (Figure 2), it has been observed that the calcium concentration is high in the northeast of the study area. The variation in the

concentration of magnesium in this region is similar to that of calcium. The sodium ion is one of the dominant components of the study area. The concentration of sodium varies spatially, increasing to the northeast part of the area, with higher concentrations in the eastern part of the study area indicating the influence of the Bay of Bengal. Chloride levels are a good indicator of water quality. The spatial variation of chloride could be similar to sodium (Figure 3). The quantity of nitrate and nitrite in the water should not exceed 50 mg/L as per the guidelines (Table 2) (Figure 4). The hardness of the water restricts its use for industrial purposes by starting to climb pots, boilers and irrigation pipes which can cause health problems for humans. The total hardness in mg/L is determined by the following equation (Todd, 1980):

$$TH = (Ca^{2+} + Mg^{2+}) \text{ meq/l} \times 50$$

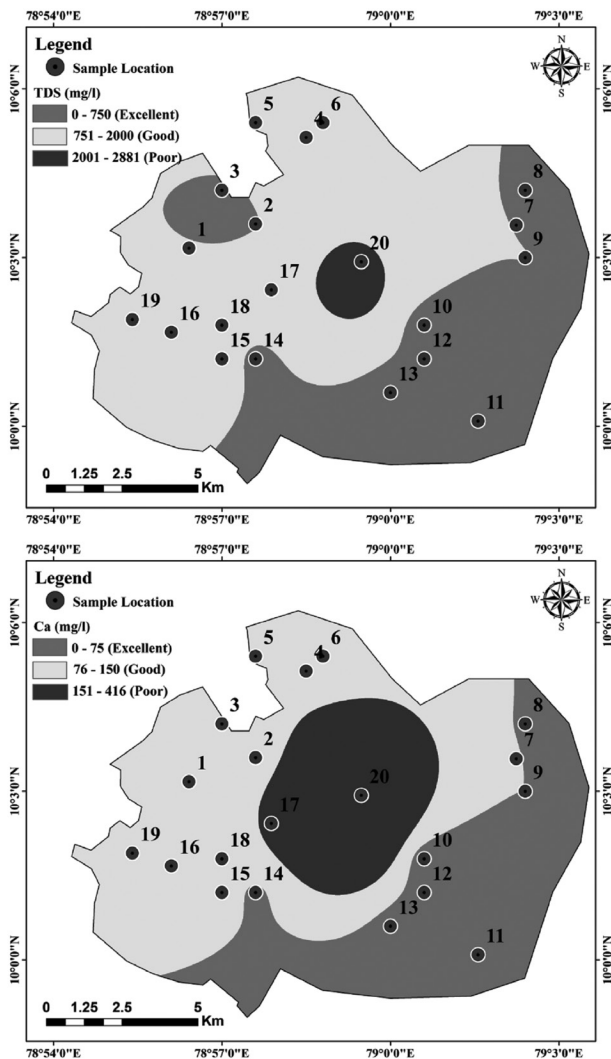


Figure 2: Spatial distribution of TDS and Ca.

The calculated total hardness (TH) values range between 60 mg/L and 1040 mg/L with a mean value of 250.4 mg/L and 40% of the samples represent soft to moderate level of groundwater hardness. It is found that the hardest groundwater falls in the northeast part of the study area (Figure 5). Alkalinity indicates the acid neutralising capacity of water. Because carbonate rocks are an important source of alkalinity therefore alkalinity is linked to hardness.

The Piper diagram (Figure 6) was developed using analytical data obtained from hydro chemical analysis. It was developed to understand and identify the water system in different classes. This explains the difference or dominance of cations and anions in the study area. Ca^{2+} type dominates the groundwater of the study area. The percentage of samples falling under the Ca^{2+} to Mg^{2+} category is 85% in the region. Some samples

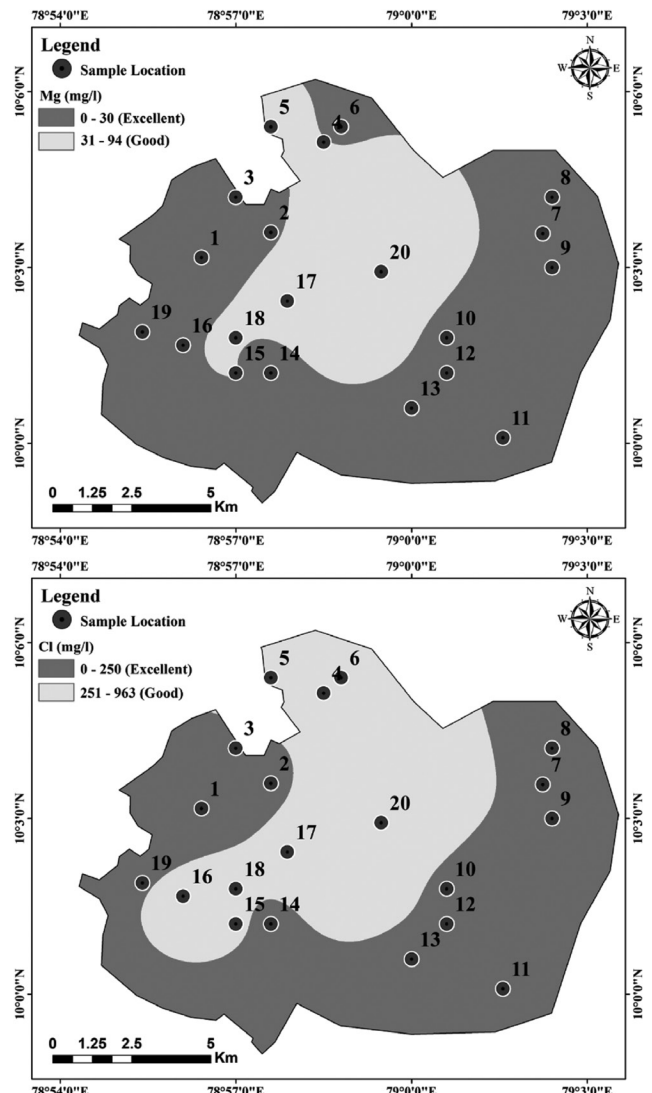


Figure 3: Spatial distribution of Mg and Cl.

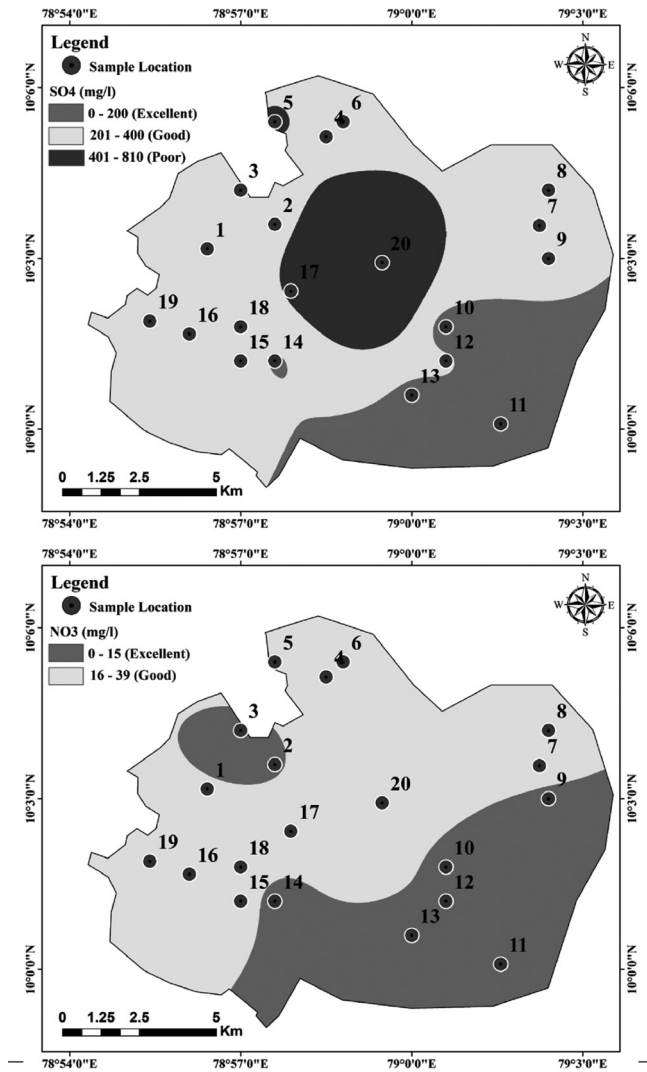


Figure 4: Spatial distribution of SO_4 and NO_3 .

were spotted in calcium and chloride type. According to Gibbs' plot (Figure 7), many samples fall between 100 and 1000 TDS in the region, so this refers to the contact between rock and water, which is the main factor controlling the groundwater quality in the study area (Gibbs, 1970). The relatively low concentration of carbonate minerals in the study area indicates the main origin of Ca^{2+} and Mg^{2+} from silicate weathering. Bicarbonate is one of the abundant anions in the groundwater samples and the carbonate concentration is in below detectable limit.

The quality of groundwater for irrigation is determined by the sodium absorption rate (SAR) $\text{Na}\%$ and RSC values (Table 3). The effects of irrigation water and soil infiltration rates depend on the relationship between the flocculating effects of specific behaviour and the scattering effects of sodium. SAR values were classified as excellent (<10), good (10-18), doubtful (18-26) and

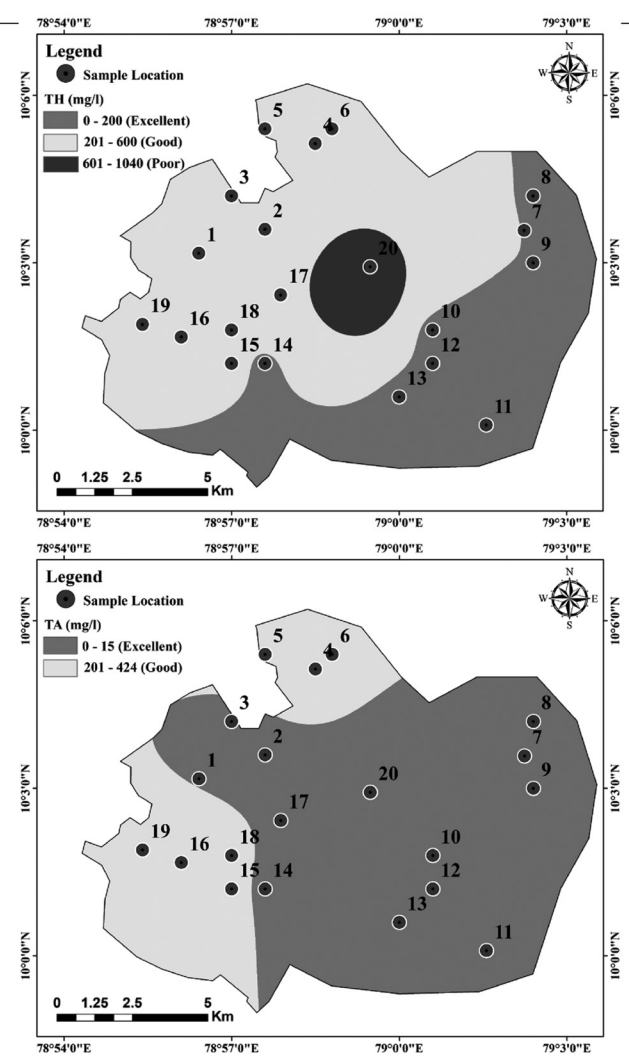


Figure 5: Spatial distribution of TH and TA.

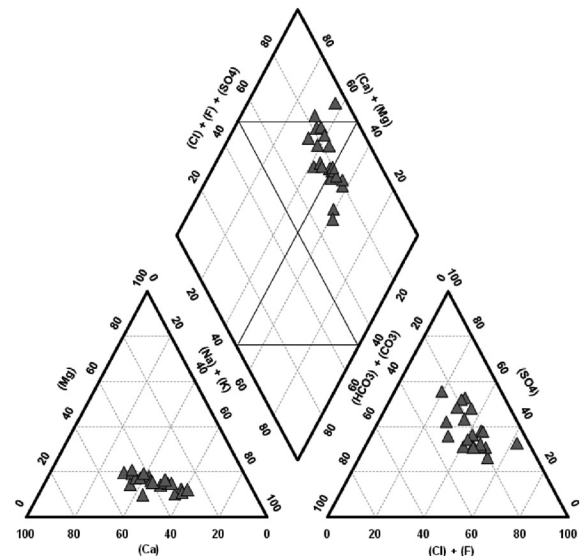
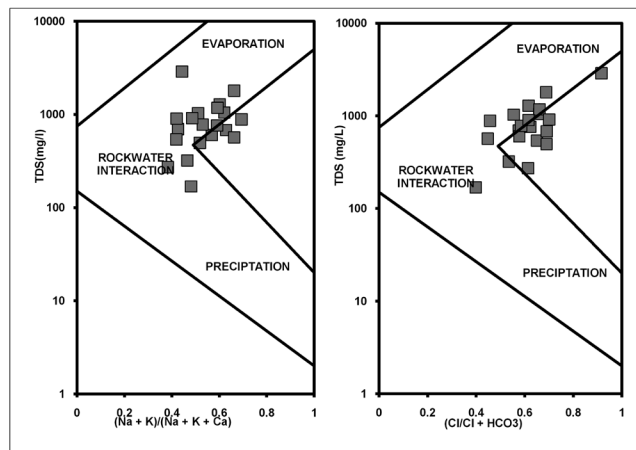


Figure 6: Piper trilinear plot shows hydrogeochemical facies of the groundwater samples.

Table 3: Groundwater quality based on suitability of water for irrigation purposes

Parameters	Range	Class	Sample	
			No .sample	% sample
EC	<250	Excellent	1	5
	250–750	Good	3	15
	750–2,000	Permissible	14	70
	2,000–3,000	Doubtful	1	5
	>3,000	Unsuitable	1	5
Na%	<20	Excellent	10	50
	20–40	Good	10	50
	40–60	Permissible	Nil	Nil
	60–80	Doubtful	Nil	Nil
	>80	Unsuitable	Nil	Nil
MR	<50	Suitable	20	100
	>50	Unsuitable	Nil	Nil
TH	<75	Soft	2	10
	75–150	Moderately	7	35
	150–300	Hard	10	50
	>300	Very hard	1	5
RSC	<1.25	Safe	20	100
	1.25–2.5	Marginally suitable	Nil	Nil
	>2.5	Not suitable	Nil	Nil
SAR	<10	Excellent	20	100
	10–18	Good	Nil	Nil
	18–26	Doubtful	Nil	Nil
	>26	Unsuitable	Nil	Nil
KI	<1	Suitable	20	100
	>1	Unsuitable	Nil	Nil
TDS	<500	Desirable for drinking	4	20
	500–1000	Permissible for drinking	10	50
	1000–3000	Useful for irrigation	6	30
	>3000	Unfit for drinking and irrigation	Nil	Nil
TA	<200	Suitable	20	100
	>600	Unsuitable	Nil	Nil

**Figure 7: Gibbs plots show mechanisms controlling the groundwater chemistry.**

unsuitable (>26) for irrigation (Wilcox, 1955) and in the study area, SAR value shows that 100% of samples fall in the field of excellent for irrigation.

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$

Sodium hazard is an important parameter for determining groundwater suitability for irrigation because it is a measure of alkaline or sodium risk to crops. This result indicates that there is no alkaline risk to the crops in the study area, however, it shows the presence of high levels of salinity in the groundwater. Those 15% and 70% of the samples were compiled into C2S1–C3S1 (Figure 8). The result has shown about 50% of the groundwater samples are excellent and 50% of samples are good for irrigation purposes. The values of Na% show a mismatch with the EC values given the Wilcox's chart (Figure 9) (Packialakshmi and Ambujam, 2011).

$$Na\% = \frac{(Na^+ + K^+) \times 100}{\sqrt{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)/2}}$$

RSC (residual sodium carbonate) is one of the most important parameters; it has been used to determine irrigation water suitability. If the concentration of carbonate and bicarbonate is higher than the concentration of calcium and magnesium, it will affect the fertility of the soil and the growth of plants (Brindha et al., 2013). RSC values are classified as <1.25 meq/L is safe, 1.25–2.5 is marginally suitable and >2.5 is not suitable for irrigation purposes. The RSC values show that 100% of samples fall in the field of excellent category.

$$RSC = (HCO_3 + CO_3) - (Ca + Mg)$$

PI (Permeability Index) diagram shown in Figure 10 (Doneen, 1964) reveals the division of water quality into three types based on PI and total salt concentration. Class I indicate the 100-75% permeable, that is suitable for irrigation. Class II is indicated as 75-25% permeable and it is moderately suitable for irrigation purposes. Class III is <25% permeable and it is shown unsuitable for irrigation purposes. The final class III is >25% permeable and has been shown to be unsuitable for irrigation purposes. Figure 10 shows that 90% of the samples fall into class I & II, and the remaining 10% in the third class.

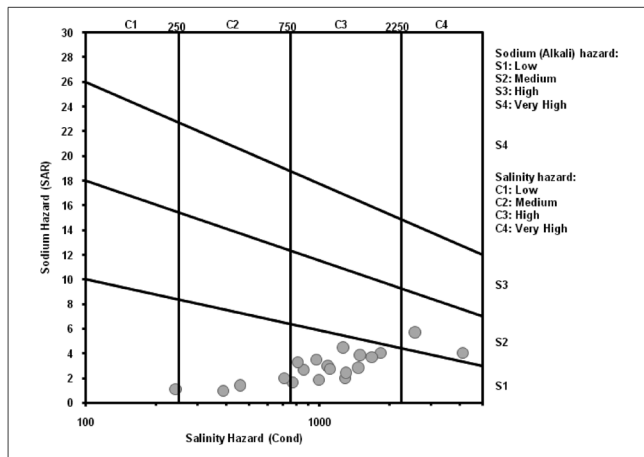


Figure 8: USSL plots show the irrigation water quality based on sodium and salinity hazard.

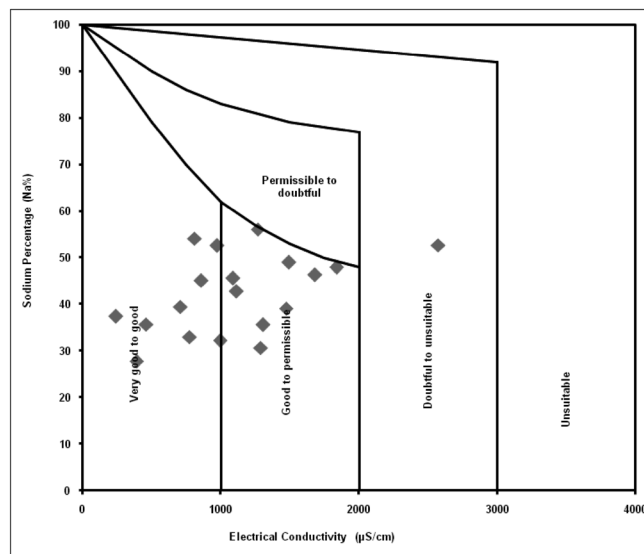


Figure 9: Plots show the Na% vs. EC for irrigation water quality.

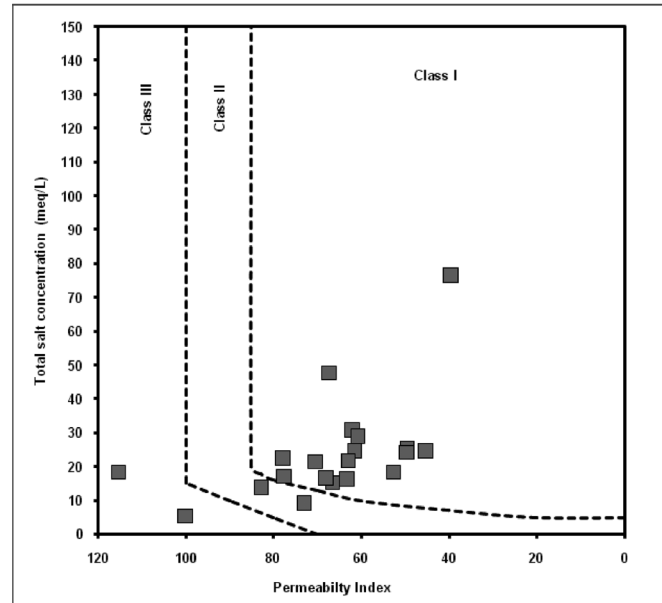


Figure 10: Doneen's PI plot for irrigation water quality classification for soil permeability.

$$PI = \frac{Na + HCO_2}{Ca + Mg + Na} \times 100$$

Ca^{2+} and Mg^{2+} generally maintain equilibrium in most groundwater (Hem, 1985). Excess Mg^{2+} in groundwater during equilibrium can adversely affect soil quality, causing it to become alkaline, resulting in reduced crop yields (Kumar et al., 2007). Paliwal (1972) has developed an index code for calculating magnesium hazard (magnesium ratio as MgC). MR is calculated using the below formula:

$$MgC = \frac{(Mg^{2+}) \times 100}{(Ca^{2+} + Mg^{2+})}$$

MgC of above 50 indicates an increase in soil alkalinity and it can adversely affect crop yields by over-fertilizing. The MgC values of all samples in the present study indicate an effect on crop yields and may exceed 50 mg/L. The Kellys index is used to classify water for irrigation purposes, sodium is measured against calcium and magnesium is considered to calculate this parameter. KI of above one (> 1) indicates the presence of high levels of sodium in water (Kelly, 1940). Therefore, water with $KI < 1$ is suitable for irrigation, while those with higher rates are unsuitable (Sundaray et al., 2009). The KI is calculated using the below formula and all the ions are expressed in mg/L. In the present study, 100% of the groundwater samples are appropriate for irrigation according to the classification.

$$KR = \frac{Na^+}{(Ca^{2+} + Mg^{2+})}$$

The correlation study is used to know the mutual relationship between two hydro chemical variables. The following interpretations are considered as the results of the correlation coefficient, a high correlation coefficient (near 1 of < 1) represents a good connection between two parameters and values around 0 indicate no relationship between the parameters. In study region, a strong positive correlation of 0.5 and above has been obtained between EC with TDS, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- ; TDS with Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- ; TH with Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- ; TA with Na^+ , K^+ , NO_3^- ; and mutual correlation has been found between Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^- . Whereas poor and no correlation were obtained between HCO_3^- and Ca^{2+} , Mg^{2+} , SO_4^{2-} except Na^+ , K^+ , while NO_3^- positively correlates with HCO_3^- . Most of the ions are positively correlated with EC and TDS (Table 4) shows such ions are derived from the same source of irrigation return flow, domestic effluent (Muruganantham et al., 2021). This trend also indicates the influence of evaporation and poor drainage conditions on the groundwater system (Bari et al., 2021). The aim of factor analysis in the present study is to define the observed relations between the chemical ions. In the present study, principal component analysis of varimax rotation with Kaiser Normalisation has been performed. Factor loadings, communalities and

Eigen values (Table 5) were examined to evaluate the variables belonging to a specific chemical process and also to find out the dominance and contribution of the major elements in the total data set. The result of the sorted rotated factor analyses for the hydrogeochemical data is summarised in Table 5. The factor loading is classified as strong (> 0.70), good (0.70–0.50), moderate (0.50–0.30) and poor (< 0.30), respectively. The factor analysis for groundwater samples extracted three factors with a total of variance about 90.61%. The first factor with 62.26% variance represented by strong loadings of EC, TDS, TH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} and NO_3^- with medium loading of HCO_3^- and negative loading of F represents influences of mineral weathering and rock water interaction along with anthropogenic activities. The third factor with an 8.00% variance signifies strong loading of F ion indicating leaching activities of apatite mineral as a source for this ion (Prakash et al., 2020).

Conclusions

The order of abundance of cations in the groundwater from the study area follows as $Na > Ca > Mg > K$ and anions are $Cl > SO_4 > HCO_3$. The groundwater quality in many parts of the Avudayarkoil block is not contaminated, as indicated by the reported parameters. The majority of samples have been found suitable for irrigation purposes as per the USSL diagram, Wilcox diagram and other agricultural indices. Permeability index values show that the groundwater quality of

Table 4: Correlation matrix for the analytical results

Results	EC	TDS	TH	TA	pH	Ca	Mg	Na	K	Cl	HCO_3	SO_4	NO_3	F
EC	1.00													
TDS	1.00	1.00												
TH	0.94	0.94	1.00											
TA	0.46	0.46	0.20	1.00										
pH	-0.17	-0.17	-0.21	-0.02	1.00									
Ca	0.94	0.94	1.00	0.20	-0.21	1.00								
Mg	0.95	0.95	0.99	0.31	-0.23	0.99	1.00							
Na	0.96	0.96	0.81	0.59	-0.12	0.81	0.84	1.00						
K	0.92	0.92	0.76	0.53	-0.13	0.77	0.79	0.97	1.00					
Cl	0.99	0.99	0.95	0.38	-0.18	0.95	0.96	0.94	0.90	1.00				
HCO_3	0.46	0.46	0.20	1.00	-0.02	0.20	0.31	0.59	0.53	0.38	1.00			
SO_4	0.97	0.97	0.95	0.40	-0.18	0.95	0.96	0.90	0.84	0.95	0.40	1.00		
NO_3	0.94	0.94	0.81	0.61	-0.01	0.81	0.85	0.95	0.89	0.90	0.61	0.91	1.00	
F	-0.10	-0.10	-0.01	-0.09	0.01	-0.01	-0.04	-0.16	-0.29	-0.14	-0.09	0.02	-0.08	1.00

Table 5: PCA with Varimax rotation and Kaiser Normalization

Parameters	Factor 1	Factor 2	Factor 3
EC	0.95	0.29	-0.07
TDS	0.95	0.29	-0.07
TH	0.99	-0.01	0.03
TA	0.20	0.96	-0.04
pH	-0.24	0.16	0.09
Ca	0.99	-0.01	0.03
Mg	0.98	0.10	0.01
Na	0.85	0.46	-0.14
K	0.82	0.41	-0.29
Cl	0.97	0.20	-0.11
HCO ₃	0.20	0.96	-0.04
SO ₄	0.96	0.22	0.07
NO ₃	0.83	0.49	-0.03
F	-0.02	-0.05	0.99
Total	8.80	2.76	1.12
% of Variance	62.86	19.75	8.00
Cumulative %	62.86	82.61	90.61

the study area is suitable for irrigation purpose in most of the regions. Groundwater samples from some locations are unsuitable for agriculture practice because of the higher values of hardness, calcium and magnesium concentrations. If this type of water is used for irrigation, it will affect the crop yield and the soil quality. In general, the impact of agricultural return flow, anthropogenic effluences, ion exchange and weathering are the sources of groundwater pollution in the study area. The local government and management must create awareness about the greater impact of fertiliser usage among the farmers and also suggest proper maintenance by controlling anthropogenic activities to reduce groundwater pollution.

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